

STRUCTURE AND RHEOLOGY OF SEMIVITREOUS PORCELAIN DURING KILNING

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Data on the rheological behavior of porcelain-group materials samples under pure shear, supplementing the results of dilatometric studies of shrinkage, were obtained. The concept of a macromechanism of deformation along critical regions was proposed to explain shear deformation at low temperatures, which is due to grains slipping (GS) along their contact boundaries. It was found that there exists a constant (with respect to the heating temperature and important to 1200°C) structural–rheological component which is responsible for the dilatation behavior due to GS. At temperatures of intense crystallization of mullite the maximum viscosity growth rate was found to correspond to the maximum shrinkage rate.

Key words: porcelain, deformation, rheology, viscosity, pure shear, mullite, kilning, liquid-phase sintering, shrinkage.

Energy conservation in ceramics technology is bound up with, first and foremost, lowering the kilning temperature and decreasing kilning time. One method used for this is to introduce active fluxes, which sometimes cause wares to deform. Three main groups of factors affect the deformation of ceramic ware: the chemical, phase and particle-size compositions of the raw materials, the uniformity of the half-finished ware, and the drying and kilning parameters (uniformity of the temperature field, gas-dynamic regime, and others).

There are many works, including [1–4], concerned with the physical-chemical processes occurring during kilning of semivitreous porcelainware containing a large amount of flux and studying the properties of the porcelain. A review illuminating modern aspects of the phenomenology of kilning porcelain is given in [5]. The most relevant studies concern the possibility of increasing the strength of porcelainware by introducing a low-activity crystalline phase and adjusting the particle-size distribution of the initial components. In the review [6], the mechanisms by which active additives act on structure formation processes in porcelain are described and the additives used in porcelain manufacture technology are divided into four classes.

Relatively few works study the deformation processes occurring semivitreous porcelainware during kilning. As a rule such studies are comparative. For example, in [7] the proneness of different types of porcelain to deformation was

studied by means of a rod supported in cantilever. The sintering and deformation of wares under the dead weight due to a change in Young's modulus of the half-finished ware are described in [8]. The authors of [9] focused on the deformation of porcelain samples under three-point bending during kilning.

Most of the experiments described above were performed by bending or compressing (stretching) the samples. The main drawback of compression and tension tests is that the deformation of wares under a load cannot be determined accurately and separately from shrinkage because these two processes interfere with one another. The volume-stress state of wares during kilning is determined mainly by the gradient of the temperature field (gradient of the shrinkage rate) and by the stress field under the dead-weight pressure. For this reason deformation under load must be studied separately from deformation due to sintering of the material. Thus, when a tangential stress is applied to a sample, for example, when the sample is twisted, volume deformation can be neglected (only the instantaneous density of the half-finished ware is meaningful). The main value of such an approach is that rheological data pertaining to pure shear irrespective of shrinkage are obtained directly. In [10] the torsion method was used to determine the viscosity of refractory clays and its relation to other properties of the samples. Unfortunately, the torsion test for determining viscosity is rarely used because the loading scheme is difficult to implement.

The objective of the present work was to compare the rheological behavior of samples with their structural changes

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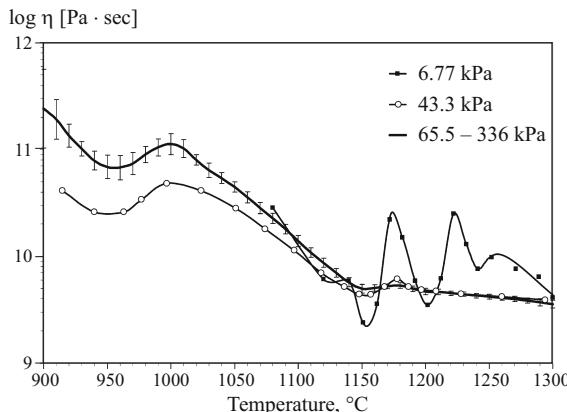


Fig. 1. The logarithm of the shear viscosity versus the temperature according to torsion experiments on thin-wall semivitreous porcelain tubes pre-kilned at 900°C for different applied shear stresses (heating rate 2 K/min; the error bars were calculated for confidence probability 0.99).

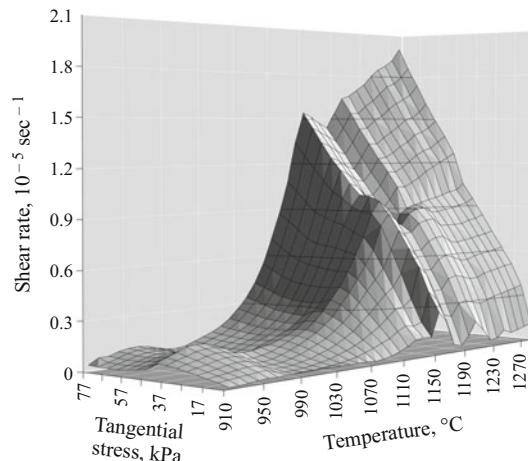


Fig. 2. Interpolated flow surface (under pure shear) according to torsion experiments on thin-wall semivitreous porcelain tubes pre-kilned at 900°C (heating rate 2 K/min).

— the phenomenology of the deformation of semivitreous porcelainware during kilning.

Three types of materials (half-finished wares) were chosen: semivitreous, sanitary-technical-technical, and household porcelain (see Table 1).

The method of twisting thin-wall tubes, which is described in [11], was used to study the rheology of half-finished wares under pure shear. The samples were formed by slip casting in the form of thin-wall tubes, pre-kilned at temperature 900°C, and tested with constant heat at the rate 2 K/min. In calculating the purely shear viscosity and other parameters, the shrinkage anisotropy of the samples was taken into account.

Aside from studying shear deformation, the deformation of samples was also determined by means of dilatometry. The samples were formed into 6 mm in diameter and 15 mm long solid cylinders by slip casting and pre-kilned at 900°C. The dilatometric studies were performed with a constant rate of heating 2 K/min using a NETZSCH DIL 402 PC contact dilatometer. The shrinkage was recorded along the axis of a cylindrical sample.

These studies showed that even though the compositions and kilning intervals were different the rheological behavior of the three experimental materials during kilning did not dif-

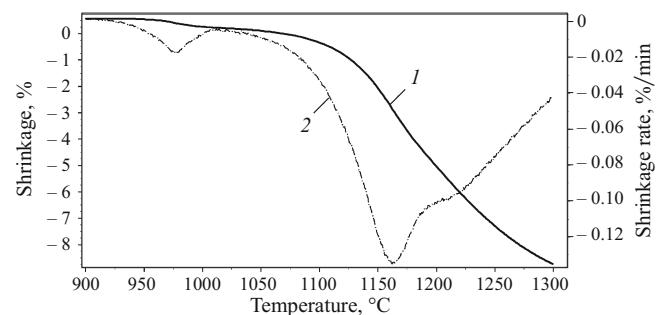


Fig. 3. Dilatometric curves of shrinkage (1) and shrinkage rate (2) for a semivitreous porcelain sample pre-kilned at 900°C (heating rate 2 K/min).

fer much, so that the parameter plots presented in Figs. 1 – 3 can be regarded as typical for the porcelain-group materials.

Electron microscopy (Supra 50 VP LEO scanning electron microscope) was used to elucidate the evolution of the half-finished structure. Chips of the half-finished samples twist tested up to a definite maximum temperature (heating rate 2 K/min, followed by cooling together with the furnace) were used. The chips were etched with a 2% aqueous solution of HF to best tint the structure of the crystalline formations.

TABLE 1. Raw Materials Composition of the Experimental Samples

| Material type | Content, wt.% | | | | | |
|--|---------------|--------|-------------|----------|-----------|---------------------|
| | Clay | Kaolin | Quartz sand | Feldspar | Pegmatite | Porcelain fragments |
| Sanitary-technical-technical porcelain | 23.5 | 28.5 | 14 | 11 | 13 | 10 |
| Household porcelain | 12.0 | 45.0 | 23 | — | 20 | — |
| Semivitreous porcelain | 29.0 | 33.0 | 18 | — | 15 | 5 |

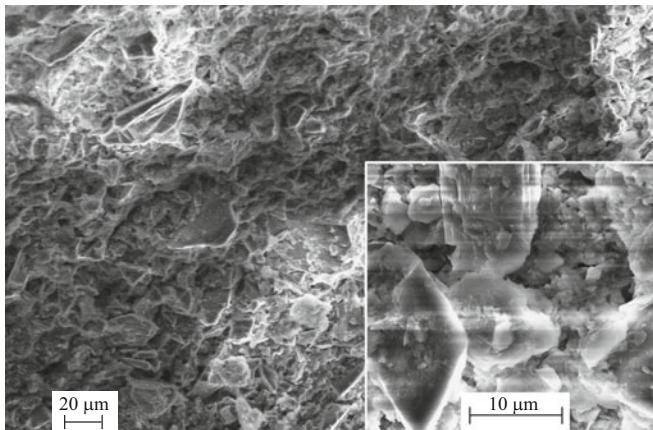


Fig. 4. Microstructure of a household porcelain sample kilned at 900°C.

The comparison of rheological behavior and shrinkage of the samples were compared with their structural changes at temperatures ranging from 900°C (preliminary temperature) to the final kilning temperature 1320°C.

The structure of samples kilned at 900°C, presented in Fig. 4, consists of relatively large fragmental particles in contact with one another. The regions between them are nonuniformly filled with smaller particles forming a loose porous structure. Heating above 900°C intensifies the sintering of the particles. The rate of sintering is limited by diffusive transfer of matter from the contact boundaries, where the matter is exposed to high pressure, into the near-contact regions of the particles. Feldspar begins to melt at 920°C [1]. Because impurities are present this temperature is low compared with the eutectic melting temperature of feldspar in the leucite – mullite – cristobalite phase diagram. Thus, the appearance of a liquid phase as a result of the partial melting of feldspar promotes an increase of the shrinkage rate (see Fig. 3). The increase of the mobility of the system up to temperature 950°C (see Fig. 1) attests to an increase in the amount of the liquid phase. It is well known that the equivalent sintering stress (effective stress of hydrostatic compression) due to capillary pressure depends not only on the nature of the interacting phases but also to a large extent on the fineness of the components. For this reason it can vary over wide limits and reach quite high values — from 0.1 MPa for compacts from glass powders [12] to 20 MPa for nanocrystalline zirconium dioxide [13]. On the one hand capillary pressure promotes shrinkage and on the other hand it limits particle motion (organizes a definite structural order) and decreases the mobility of the diffusion layer separating the grains on the other. For this reason it is a force that can greatly increase the shear viscosity of the material (Fig. 5). From the standpoint of mechanics such a decrease of the mobility of the diffusion layer is similar to the increase of the external friction force with increasing applied normal pressure. In this case the viscosity η of the material will be a function of the friction coefficient k between rigid particles and of the viscosity η_L of the liquid phase:

$$\frac{1}{\eta} = \frac{1}{Ck + L_C \eta_L} + \frac{1}{L \eta_L},$$

where $1/\eta$ is the flowability of the material, the first term on the right-hand side of the equation is the flowability of a system of rigid particles in contact with one another, the second term is the flowability of liquid-phase interlayers, C is the effective fractional contribution of the friction coefficient with rigid contact between the particles, L is the effect fractional contribution of the viscosity of the free (between agglomerates) liquid phase, L_C is the effective fractional contribution of the viscosity of the near-contact liquid phase, where C , L , and L_C depend on the porosity, liquid-phase fraction, and other factors; the friction coefficient k is directly proportional to the equivalent sintering stress and does not depend on the area of the slip surfaces but it is related with the physical-chemical parameters of the slip planes.

It cannot be ruled out that at this stage (approximately to 980°C) the sample also shrinks because of compaction of the quite loosely packed product of dehydration of kaolinite, starting from even lower temperatures (below 900°C).

The shrinkage can be due to the decomposition of meta-kaolin. The thermogram of kaolin [2] shows an exothermal effect in the range 930 – 1050°C. The prevailing opinion [14] is that this thermal effect is due to the decomposition of meta-kaolin into aluminosilicate spinel $2\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ and amorphous silica at a temperature of about 925°C. Evidently, the eutectic surroundings of the meta-kaolin particles strongly affect the temperature and intensity of the decomposition. Dana and Kumar have observed [4] that in porcelain meta-kaolin transforms into a spinel type structure and amorphous silica in the range 950 – 1000°C. Dannert, et al. [3] believe that not only amorphous silica and a spinel type phase but also nano-size primary mullite form from meta-kaolin almost simultaneously starting at 920°C.

Raising the temperature from 900 to 1000°C does not lead to any structural changes (Figs. 4 and 6), while the curves of the viscosity (Fig. 1) and the shrinkage and its derivative (see Fig. 3) attest to processes occurring in the struc-

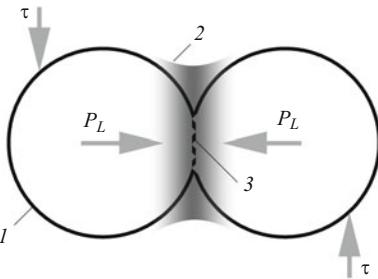


Fig. 5. Diagram of the contact between solid grains of relics [τ] applied shear stress, P_L) effective stress due to sintering]: 1) grain; 2) liquid phase; 3) slip plane.

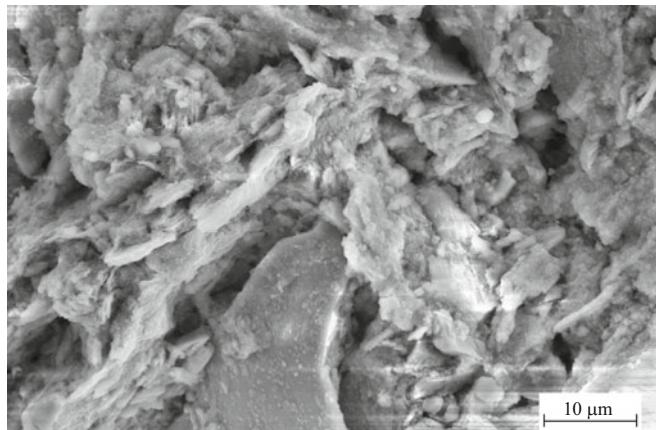


Fig. 6. Microstructure of a household porcelain sample kilned at 1000°C.

ture that affect its mechanical properties. An important fact is that the shrinkage and viscosity growth rate both reach their maximum values at 980°C. It can be supposed that the viscosity increase could be due to structural hardening of kaolinite relics at the expense of the phases formed as well as to densification as a result of their shrinkage.

The large number of microcracks in the structure of the material facilitates the deformation of a sample during the shrinkage process. These cracks appear a result of not only nonequilibrium processes preceding kilning but also active decomposition and nonuniform heating processes. Because the concentration of microcracks and open pores is high a branched network of defects forms in the structure of the material. For this reason semivitreous porcelain can be imagined simply as consisting of relatively large blocks (conglomerates) of different particles which are tied to one another by intermediate “links” — mainly kaolin relics. It is obvious that these (critical) regions are stress concentrators and deformation under force moments accompanying an externally applied mechanical load will occur largely in them. This will result in volume (shrinkage) and shear (irrespective of the form of an anisotropic load on the material) deformation of the sample.

Thus, a “bending according along critical regions” principle can be formulated as follows. Conglomerates or their blocks held in place relative to one another by the intermediate regions, which easily undergo shear deformation under an external load or internal stresses as old microcracks “heal” and new ones, undergo shear displacements (turns). From the standpoint of mechanics “bending along critical regions” occurs quite easily, and it is a macromechanism of diffusive transfer. This makes it necessary to take account of the complicated spatial character of the deformations.

An analogy can be drawn to curves of flow under stress above the critical value 10 MPa, which can be designated as the ultimate yield point in the experimental temperature range (see Fig. 2). Interestingly, just as a radical structural change of the material under heating, the physical-chemical

processes giving rise to extrema in the viscosity curves (see Fig. 1) have practically no effect on the characteristic features of the flow curves (excepting a change of the yield point) above the critical stresses. Therefore, there must exist in the experimental rheological system a fundamental constant structural component that determines its rheology, specifically, the dilatation behavior. This component could be the slip (shear) planes, determining a unified collection of flow mechanisms in the entire experimental temperature interval; here, the structure of the slip planes must not change under heating. In the experimental rheological system the surfaces of solid particles (for example, mullite grains) can form such a structure on account of the more mobile diffusion layer at their locations of contact (see Fig. 5).

The structure of the diffusion layer can be represented by a two-dimensional model “quasi-liquid phase” whose rheology remains unchanged in a large temperature interval. The parameters of such behavior will depend on the degree of structural ordering, correlating with the heating temperature of the material and the chemical composition.

The flow curves obtained at temperatures 910 – 950°C (see Fig. 2) have two rectilinear sections where stress has virtually no effect on the viscosity, i.e., the straight lines are characterized by Newtonian flow (their extrapolation intersects the origin of coordinates). The first rectilinear section reflects the flow of a liquid-like system. Such a flow is possible for relatively low stresses, when there is enough time for the structure to change without its wholeness being destroyed (creep). The rapid decrease of the deformation rate near the stress 45 kPa is due to a transition to a different mechanism of deformation and must occur as a result of “avalanche” binding of the structure of the contact diffusion layer.

Subsequent increases of the shear stress will probably destroy the structure formed, which is stable only in a narrow range of stresses. A temperature rise will increase the structural disordering of the diffusion layer. Thus, the difference between its rheological response to different mechanical stresses will decrease, as can be seen by comparing the deformation curves (difference of the slope angles of the first and second rectilinear sections), for example, those obtained at 930 and 1230°C (see Fig. 2).

The nominal yield point of 2 – 6 kPa and higher in the temperature interval from 960 to 1120°C, the maximum value 10 kPa being reached at 1000°C. The appearance of a nominal yield point corresponds to the decomposition onset temperature of meta-kaolin (950°C, according to the data of [4]), while the decomposition completion temperature of meta-kaolin (100°C, according to the data of [4]) corresponds to the maximum nominal yield point. Meta-kaolin decomposition produces the strongest possible structure with a small number of nanocrystalline mullite grains precipitating out.

Microcracks (marked by broken lines) are clearly visible in the photograph of the microstructure of samples kilned at 1000°C (Fig. 7). Their length and connectedness attest to an

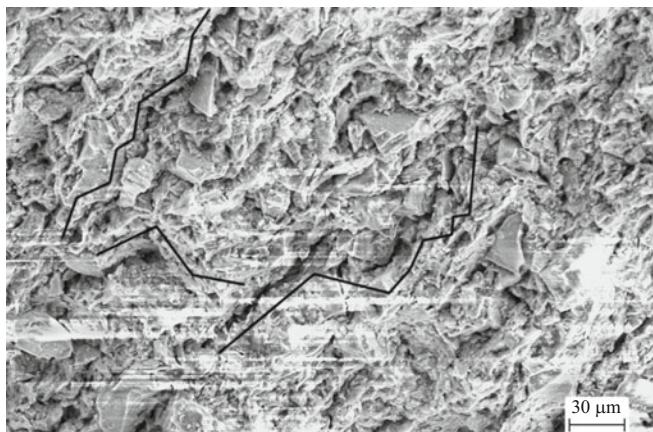


Fig. 7. Microstructure of a sample of household porcelain, kilned at 1000°C, with an extended system of cracks (underscored by broken lines).

extended system of interconnected pores and microcracks within the volume of the system. The conglomerates, which evidently consist of clayey particles, have a layered structure (see Fig. 6), while the pores in the material do not have the characteristic shape, because they represent gaps between formless comminuted particles.

Pseudoplastic rather than thixotropic behavior manifests near temperature 1000°C. This phenomenon could be due to the fact that as the shear stress increases asymmetric grains of primary mullite gradually become oriented with their long axes oriented along the direction of shear, thereby decreasing the viscosity. As temperature increases, their role in the rheology of the system decreases because of their possible orientation in the direction of shear, partial dissolution, increase in the amount of the liquid phase, and other factors creating conditions for a nominal yield point of 2 kPa at temperature 1130°C.

Figure 8 shows on different scales the microstructure of household porcelain samples kilned at temperature 1130°C. Even though once again distinguishable changes cannot be identified visually on a relatively small scale, a more detailed magnification reveals that the structure undergoes agglomeration in this temperature range and that the particle con-

glomerates have became more separated and distinct. The pores grew larger and also became more visible. The structure of the material can be classified as large-size (about 100 μm, predominately feldspar relics) and medium-size (20–5 μm, predominately quartz relics) splintered particles and agglomerates (50–2 μm, kaolinite relics) partially consisting of small nearly spherical (see Fig. 8) particles and branched slit-shaped pores.

The agglomerates consist of relatively large clusters (see Fig. 8) — substrates in which a texture consisting small mullite particles (about 0.04 μm) can be identified (not seen in this photograph) and uniform quasispherical particles (about 0.3 μm, presumably consisting of amorphous mullite) nonuniformly distributed in the substrate and on its surface. The shrinkage curve (see Fig. 3) shows that intensive compaction proceeds in porcelain at this temperature.

Subsequent heat-treatment to temperature 1180°C brings about a considerable change in the structure of the material (Fig. 9). While the relative similarity of the conglomerates is preserved the quasispherical particles mentioned above are no longer seen. Plots of the viscosity (see Fig. 1) and shrinkage rate (see Fig. 3) have characteristic minima (at 1150 and 1165°C, respectively), which attest to qualitative changes in the mechanical properties of the kilned material. The temperature at the viscosity minimum is also the melting temperature of potassium feldspar (1150°C, according to the data of [2]), which is well known to melt incongruently with high-viscosity silica-rich melt precipitating. As temperature increases needle crystals of secondary mullite grow in this melt.

The feldspar relics in the series of photographs of the structure of the sanitary-technical porcelain samples kilned at 1180°C are still only partially vitrified, and the melt edge surrounding the feldspar relic fragments is visible. Relatively low-density accumulations of growing mullite needle crystals (about 0.5 μm) are distributed nonuniformly in the vitrified sections, and stick-shaped formations (up to 1 μm long), which could be the result of the decomposition of feldspar, are also visible.

On account of the growth of mullite crystals the viscosity of the material increases quite sharply starting at temperature

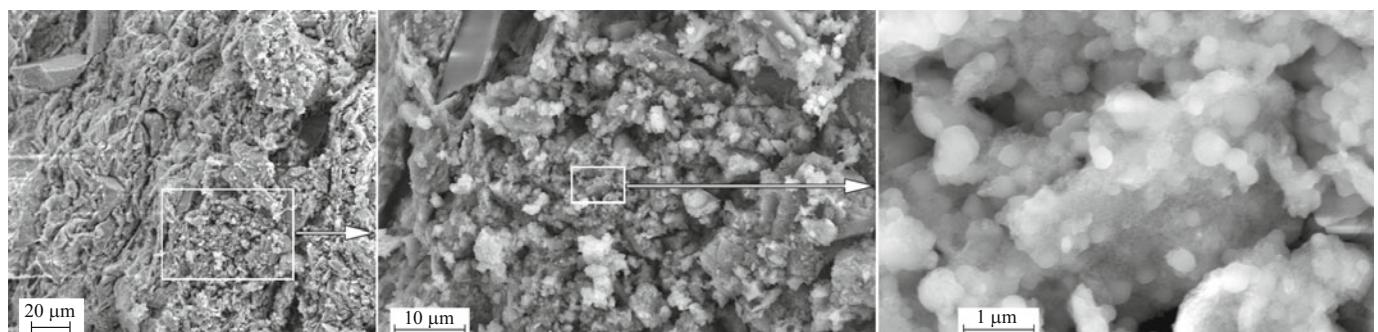


Fig. 8. Different levels of the microstructure of a household porcelain sample kilned at 1130°C shown in photographs made on different scales.

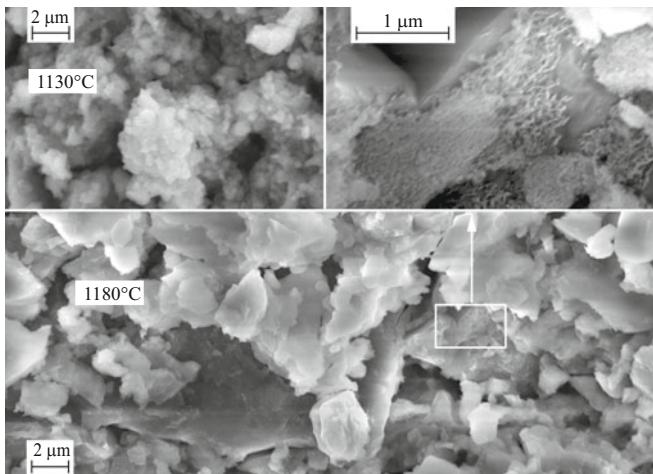


Fig. 9. Comparison on the same scale of the microstructure of household porcelain samples kilned at 1130 and 1180°C. Noticeably grown mullite crystals are seen in the enlarged fragment and it is evident that the spherical particles existing at 1130°C are absent.

1150°C (see Fig. 1) and reaching its maximum value at 1175°C, which is especially evident on the curves obtained with critical shear stresses (< 10 kPa). This attests to competition between the formation and decomposition of a framework consisting of crystalline embryos (the intensity of the latter is higher for relatively high shear stresses) in the interval 1150 – 1175°C.

The shrinkage rate starts to decrease at the temperature of the second maximum (1162°C). This could be due to silica melt, whose viscosity slowly decreases on heating, formed when potassium feldspar melts [2]. The slow decrease of the viscosity of the silica melt is manifested on the viscosity curves corresponding to high stress as a rectilinear section with smaller slope compared with the section in the region 1010 – 1150°C.

After the feldspar particles melt (1150 – 1250°C) a quite uniform structure with closed pores, whose average diameter is approximately 10 μm, forms. The total pore volume is approximately three times smaller than the volume of the quartz. For critical shear stresses (≤ 10 kPa) a viscosity maximum appears in the temperature range 1200 – 1220°C; this peak corresponds to the more gently sloping section of the shrinkage rate curve. Presumably, this is associated with the crystallization of amorphous silica into cristobalite (exothermal effect appearing in the thermograms in the range 1180 – 1250°C when kaolin is heated [2]).

Even though the hardening temperatures are different the final structure of household, sanitary-technical, and semivitreous porcelain does not show any big differences. After feldspar melts, up to the final kilning temperature (1300 – 1350°C) the main structural links of the material showing the strongest deformation resistance are quartz relics which have a relatively rigid amorphous silica-rich edge and are bound together by high-viscosity continuous kaolinite relic formations (Figs. 11 and 12). The kaolinite relics are filled rela-

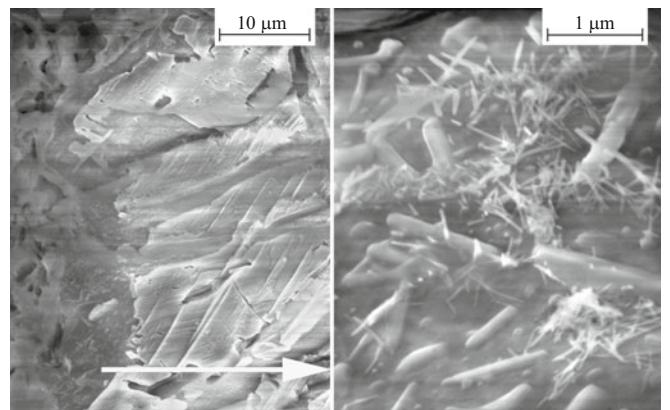


Fig. 10. Microstructure of a sanitary-technical porcelain sample kilned at 1180°C.

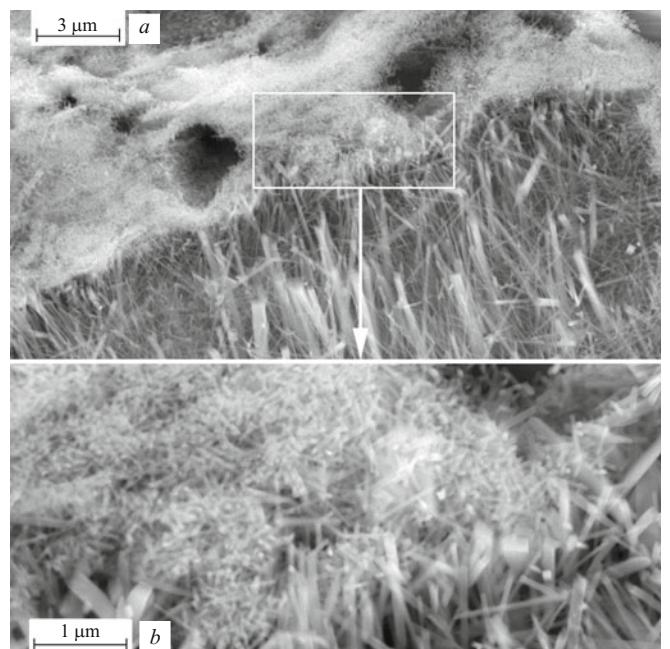


Fig. 11. Microstructure of a semivitreous porcelain sample kilned at 1300°C. The diffuse nature of the boundary of the feldspar relic and kaolinite relics enveloping its matrix is clearly visible (a). The kaolinite relics are relatively densely filled with chaotically arranged needle crystals of primary mullite (b).

tively densely with chaotically distributed 0.2 μm needle-shaped crystals of primary mullite. Some kaolinite relics retained their shape contour and the ordered linear texture of the initial particles. An obvious orientational ordering (in the diagonal direction in Fig. 12) of the quartz and feldspar relics and prolate pores, similar in nature of that observed for semivitreous ware, is seen. In some feldspar relics mullite needles are predominately oriented along the normal to the relic boundaries. On the whole feldspar relics comprising shapeless regions of melted glass penetrated by quite long mullite needles (2 – 7 μm) occupy a two to three times larger volume than the quartz relics, and their viscosity is relatively

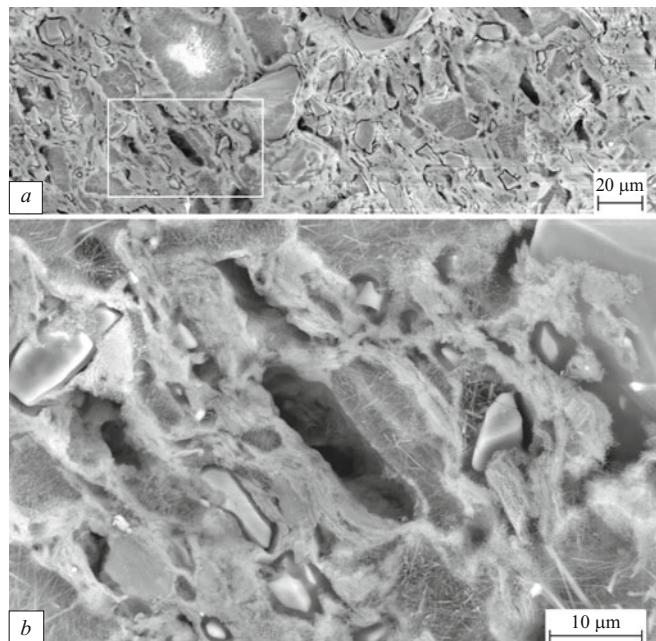


Fig. 12. Microstructure of a sanitary-technical porcelain sample kilned at 1320°C: *a*) ordered orientation of pores and relics; *b*) diffuse boundaries of touching grains (quartz, feldspar, and kaolin relics) and clearly distinguishable pore shapes (at the center of the photograph).

low. It should be noted that at the start of kilning the boundaries of touching grains (quartz, feldspar, and kaolin relics) have sharp interfaces, which on heating (interaction, decomposition, and melting of particles) become diffuse toward the completion of kilning. In the course of kilning the pores decrease the area of their own boundaries and ultimately acquire clearly distinguishable shapes (see Fig. 12).

This research has established that when semivitreous porcelain-group wares are kilned different mechanisms predominate in shrinkage and shear deformation. At low kilning temperatures (900 – 1200°C) shear deformation occurs by means of grains slipping along their contact boundaries in accordance with the proposed macromechanism of deformation along critical regions. At temperatures above 1160 – 1200°C, because of the high liquid-phase content, viscous flow processes predominate. On the other hand material shrinks by diffusion mass-transfer mechanisms: compaction of relatively loosely packed meta-kaolin and its products of decomposition during sintering of its substructure particles and gradual melting (smoothing of the surface relief) of feldspar particles and quartz grains. The decomposition of meta-kaolin (950 – 1000°C) and potassium feldspar (1150 – 1175°C) accelerates volume deformation (shrinkage) but has the opposite effect on shear deformation, increasing the effective viscosity.

It has been found that there exists a constant (with respect to the heating temperature) structural component that is responsible for the dilatation behavior up to 1200°C due to grains slipping along their contact boundaries.

On the basis of the proposed principle of the slip planes we believe that on the one hand capillary pressure gives rise to shrinkage (as is well known) and on the other hand acts as a force that can greatly increase the viscosity of the material under shear.

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